24

PROTON MAGNETIC RESONANCE INVESTIGATIONS ON PENTAERYTHRITOL

R. C. GUPTA

Department of Physics,

Lucknow University, Lucknow, India

(*Received August* 2, 1967; *Resubmitted November* 1, 1968)

Samples of pentaerythritol have been studied in a field of about 6000 oersteds using the standard bridge technique, between 94°K and 475°K, giving information about the molecular structure and motions and the diffusion of water molecules as an impurity in the solid. The measured second moment at rigid lattice temperature, namely, below 94°K, is consistent with a molecular structure having symmetry properties of the space group $\overline{I}4$ tetrahedral bond angles, C-C bond length of 1.50Å, C-O bond length of 1.46Å and C-H bond length of 1.09Å with two molecules in a unit cell in a body-centred tetrahedral crystal structure, cell dimensions being $a = b = 6.07$Å and $c = 8.74$Å in which the hydroxy-hydrogen is closer to O_1 at (x, y, z) than to O_2 at $(y, \bar{x}, \bar{z})$ as shown in figure 1.

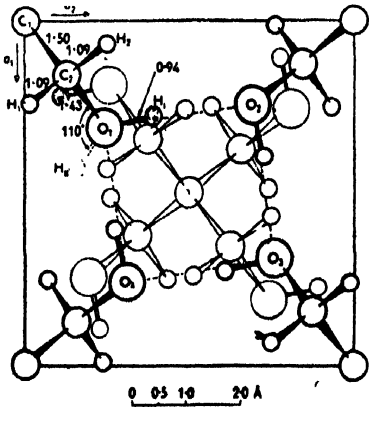

Figure 1. Pentaerythritol model showing the position of hydroxy-hydrogen.

It was found that the fractional coordinates of the position of hydroxy-hydrogen assigned by Hvoslef (1958) in his neutron diffraction study are not consistent with his diagram. This error was discovered when an abnormally high value of intramolecular contribution of about 45 gauss was obtained with the fractional

coordinates determined by him. The revised fractional coordinates are given in the following table.

	x	y	z
H_A	0.271	0.392	0.003

Carefully scaled models of the type of molecule shown in figure 2 were made using the revised coordinates for the hydroxy-hydrogen and the theoretical value of the second moment (27.02 ± 1 gauss^2) thus obtained was found to be in good agreement with the experimental value (28.1 gauss^2).

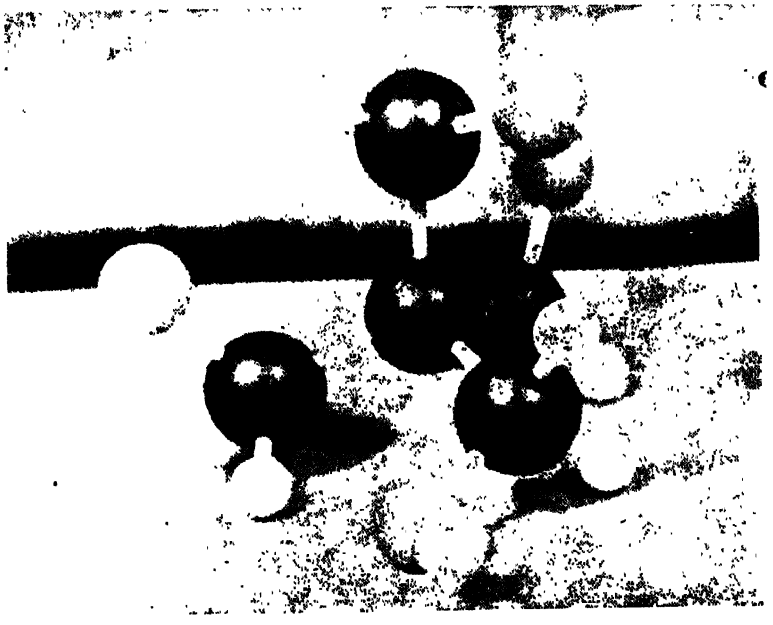

Figure 2. Molecular structure of Pentaerythritol. The atoms are labelled as follows : Black = Carbon Grey = Oxygen, White = Hydrogen.

On warming from 94°K to 233°K, a suspicion of a secondary hump appeared on the absorption spectrum, which became more pronounced at 268°K with a dip in the observed value for the second moment and the line width. Round about 434°K, the second moment and the line width diminish to a value which suggests the possibility of the reorientation of molecules. The rotation of the molecules was found to be about an axis which is the symmetry axis. At about 453°K, the second moment and the line width fall very sharply to values which indicate another transition in the solid state. The plateau GH (figure 3) has a mean value of the measured second moment of nearly 0.5 gauss which appears to

be entirely intermolecular in origin. The sharp fall in second moment from about 17.5 gauss^2 to about 0.5 gauss^2 and in the line width from about 12.2 gauss to 1.5 gauss is accompanied by a change in the crystal structure from tetrahedral to cubic which was first observed by Ebert (1931) at about 453°K.

There is a liquid like narrowness of the line in the high temperature modification as reported by Ebert (1931) and Nitta *et al* (1950) using different methods, suggesting that molecules have a considerable freedom of rotation, causing the intra-molecular contribution to the second moment to become negligibly small The theoretical value for the second moment for the general reorientation is found to be in good agreement with the observed one.

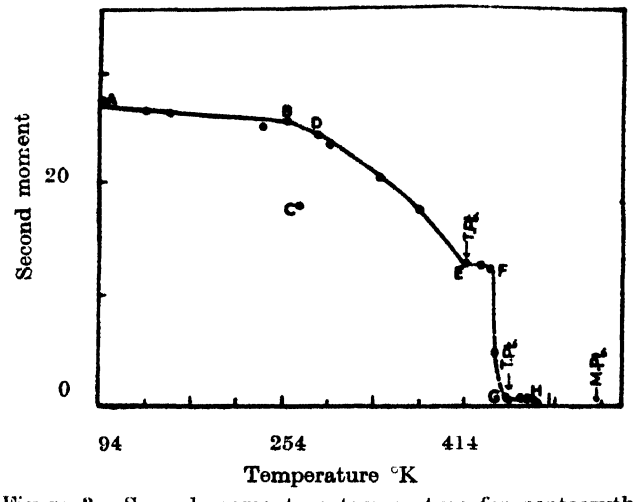

Figure 3. Second moment *vs* temperature for pentaerythritol.

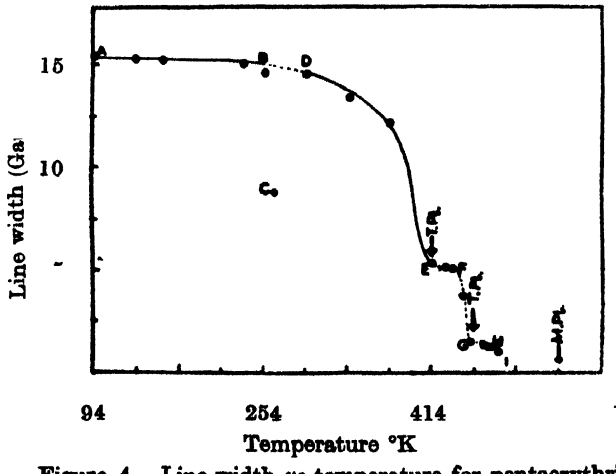

Figure 4. Line-width *vs* temperature for pentaerythritol.

There is also the possibility of diffusion of molecules through the crystal lattice supporting the effect observed in dielectric study by Kiryama *et al* (1954).

On performing the experiment again at the room temperature, after heating the sample to about 475°K, the liquid line on the top of the solid line became more sharp, which is attributed as due to the diffusion of water molecules through the lattice. Evidence of this fact is obtained by X-ray investigations by Nitta and Watanabe (1937), and thermal studies by Nitta *et al* (1950).

It is my pleasure to thank Prof. E. R. Andrew, Head of the Department of Physics, University of Nottingham, U.K. and Dr. J. P. Llewellyn of the University College of North Wales, Bangore, U.K., where this work was done, for valuable discussions and interest in the work.

REFERENCES

Hvoslef, J., 1958, *Acta Ceysta.*, **11**, 383.
Ebert, T., 1931, *Ber*, **64**, 114.
Nitta, I., Seki, S. and Momtani, M., 1950, *Proc. Japan Akad.*, **26**, 25.
Nitta, I., Watanbe, I., Seki, S. and Momtani, M., 1950, *Proc. Japan Akad.*, **26**, 19.
Nitta, I., Seki, S., Momtani, M., Suzuki, K. and Nakagawa, S., 1950, *Proc. Japan Akad.*, **10**, 11.
Nitta, I. and Watanbe, T., 1937, *Nature*, **149**, 365.
Kiriyama, R., Yabumoto, S. and Nitta, I., 1954, *Bull. Chem. Soc. Japan*, **27**, 115.

24

NUCLEAR MAGNETIC RESONANCE OF PHOSPHORUS NUCLEI

R. C. GUPTA

DEPARTMENT OF PHYSICS, LUCKNOW UNIVERSITY, LUCKNOW, INDIA.

(*Received June* 20, 1968)

The present note reports the effect of temperature on the n.m.r. line width of polycrystalline phosphorus pentachloride. It has been found that the PCl_4^+ and PCl_6^- lines are as suspected motionally narrowed at room temperature and that on cooling the motion freezes out giving broader lines. The lines overlap at 199°K.

The nuclear magnetic resonance spectrum of a solid is much broader than that of a liquid because of the static dipolar interaction between the nuclei in the solid. The isotopic re-orientation and diffusion of the molecules average their nuclear dipolar interaction almost to zero, which might then reveal a fine structure